

Measurement of an isosbestic point in the Raman spectrum of liquid water by use of a backscattering geometry

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Measurements presented here confirm that a temperature-insensitive point occurs in the backscattered Raman spectrum from liquid water. This result, coupled with existing laboratory measurements of Raman scattering from liquid droplets, indicates that a Raman lidar measurement of cloud liquid water is feasible. © 1999 Optical Society of America

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1. Introduction

The modeling of global radiation balance must accurately address both the areal coverage of clouds and their radiative capacity. The liquid-water content of clouds is an important parameter determining how effectively a cloud can absorb or radiate electromagnetic energy. Here we present measurements confirming the existence of a temperature-insensitive point in the backscattered Raman spectrum of liquid water that makes the measurement of liquid-water content of clouds using Raman lidar more feasible.

2. Background

Water droplets in clouds are known to be nearly perfect spheres for diameters less than approximately $280\text{ }\mu\text{m}$.¹ In nonprecipitating water clouds, droplet sizes are mostly well below this; usually being $100\text{ }\mu\text{m}$ in diameter or less. The assumption that water droplets in nonprecipitating clouds are spheres is therefore generally a good one.

Various theoretical and empirical studies have been performed on Raman scattering from spherical droplets. The Raman-scattered intensity from a droplet, for a given input wavelength, can be sensitive to the droplet size. This occurs because of large

resonance features that are present at certain size parameters (size parameter is defined as the circumference of the particle divided by the wavelength of the incident light). However, these studies indicate that an averaging of the resonances occurs over a reasonably broad range of droplet sizes, and thus the intensity of Raman scattering from water droplets becomes proportional to the droplet volume.² Accordingly, the intensity of Raman scattering is proportional to the mass of water in the droplets.

Raman scattering from water droplets in clouds has been measured using lidar.³ In those measurements, a spectrally wide filter that was designed for measurements of Raman scattering from water vapor (3657 cm^{-1}) allowed a significant portion of the liquid-water band ($\sim 2800\text{--}3800\text{ cm}^{-1}$) to pass as well. Thus the Raman scattering that was due to liquid water was observed as an inadvertent enhancement of the water-vapor signal in the cloud.

The Raman spectrum from liquid water is known to be temperature sensitive. This effect has been used to quantify the temperature of water droplets in laboratory studies.⁴ However, temperature sensitivity is undesirable for an atmospheric measurement of cloud liquid-water content. The effort here was to determine if the same isosbestic point that characterizes Raman scattering from liquid water using a 90-deg scattering geometry is also present when using a backscattering geometry.

3. Isosbestic Points in the Liquid Raman Spectrum

It has been shown for a wide range of temperatures that there is a point in the Raman-scattering spectrum from liquid water that is insensitive to changes in temperature. This point is known as an isosbestic point⁵ and results because the scattering involves two competing forms of water that are in equilibrium.

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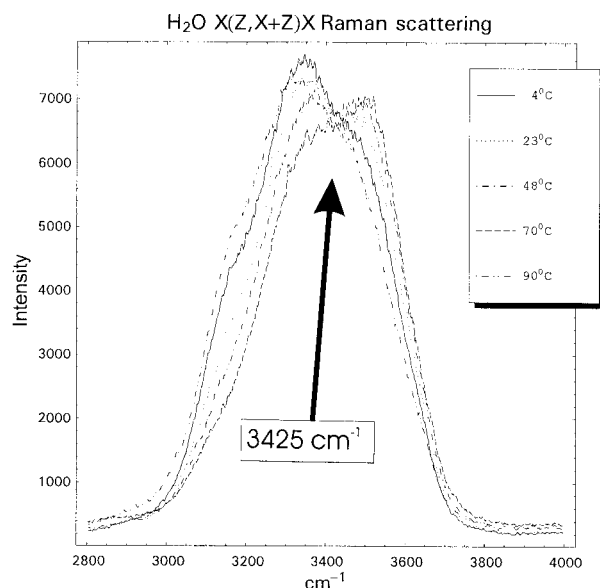


Fig. 1. Raman-scattering intensity as a function of wave number for a backscattering geometry at five temperatures: 4 °C, 23 °C, 48 °C, 70 °C, and 90 °C. The isosbestic point is at 3425 cm^{-1} as in the case of scattering at a 90-deg angle.

Above freezing, the two scattering types that are in equilibrium differ in the number of hydrogen bonds involved,⁵ whereas as the water becomes increasingly supercooled the equilibrium that dominates appears to be between a pentagonal form of water and a hexagonal form of water.^{6,7} The isosbestic point pertaining to backscattering is required for temperature-insensitive lidar measurements of cloud liquid water. However, the previous measurements made of these isosbestic points used scattering at 90 deg to the incident direction.⁵ The isosbestic point using a backscattering geometry was determined here and found to be the same as for 90-deg scattering.

The isosbestic point has been determined to occur at a shift of 3425 cm^{-1} (Ref. 5) for an incident photon traveling along the X axis with polarization in the Z direction and by measuring both the Z - and the X -polarized components of the Raman-scattered signal (i.e., unpolarized detection) along the Y axis [a configuration known as $X(Z, X + Z)Y$ that is scattering at 90 deg]. The isosbestic point was evaluated over the range of temperatures of 3 °C to 72 °C. For this range of temperature, the isosbestic point was determined to be only a function of the polarization of the incident and scattered photons that are detected. It was also shown that the isosbestic point can be determined from the polarizability tensor elements for liquid water.⁵ The tensor elements are the same for any direction of scattering, thus the isosbestic point should not be a function of scattering direction. To confirm this, the isosbestic point of liquid water was determined using a backscattering geometry $[X(Z, X + Z)X]$ over a range of temperature of 4 °C to 90 °C as shown in Fig. 1.

The laser used was a Coherent Model CR 12HD argon laser (488 nm), and the backscattered light was polarization scrambled and spectrally separated using an Instruments SA Jobin-Yvon RAMANOR HG-2S holographic grating double monochromator operated with 5-cm^{-1} resolution. The signal was detected using a thermoelectrically cooled Hamamatsu R 636-10 photomultiplier tube. The results of this backscattering experiment exhibit the same 3425-cm^{-1} isosbestic point as for scattering at 90 deg. Thus a spectrally narrow filter centered at the 3425-cm^{-1} isosbestic point would allow for temperature-insensitive measurements of cloud liquid water to be obtained using the Raman lidar technique.⁸ An actual implementation of a cloud liquid-water measurement must account for such factors as filter width, cloud penetration depth, and multiple scattering, which are beyond the scope of this paper.

4. Summary

Measurements presented here confirm that an isosbestic point in the Raman-scattering spectrum from liquid water exists at 3425 cm^{-1} for a backscattering geometry over a range of temperatures of at least 4 °C to 90 °C. Other research has shown that the intensity of Raman scattering from spherical droplets is, when averaged over a range of droplet sizes, proportional to the total droplet volume. Based on these facts, a temperature-insensitive measurement of cloud liquid water should be possible using the Raman lidar technique.

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